

EXPERIMENTS WITH A STRATOSPHERIC GENERAL CIRCULATION MODEL

III. LARGE-SCALE DIFFUSION OF OZONE INCLUDING PHOTOCHEMISTRY

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ABSTRACT

As a continuation of the previous experiments in this series, the 18-vertical-level general circulation model was used to investigate the large-scale diffusion of a further two tracers in the stratosphere. In the present experiment both tracers were initiated as photochemical ozone distributions, one distribution being based on photochemistry in an oxygen-only atmosphere, the other on photochemistry in an oxygen-hydrogen atmosphere. Photochemistry was included in the subsequent diffusion so that a joint photochemical-dynamical study resulted. The diffusion process was followed for 185 model days when the experiment was terminated, even though the tracer distributions had not attained a steady state. Despite this, substantial qualitative agreement was obtained with observation, particularly as regards the accumulation of ozone in the lower stratosphere at extratropical latitudes. The results also suggest that photochemistry for an oxygen-hydrogen atmosphere may be the more applicable to the actual atmosphere.

Both the meridional circulation and the eddies were important in the diffusion of the tracers, although they did not constitute as interactive a system as in the previous experiment. The direct meridional circulation at low latitudes was found to be the prime mover in the polewards transport of the ozone, the eddies continuing this transport polewards from the subtropics. Owing to photochemical dampening of the ozone concentration gradient, the eddies were of minor importance at low latitudes.

A schematic diagram summarizing the principal features of the large-scale diffusion mechanism is given.

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1. INTRODUCTION

Ozone, O₃, is a minor constituent of the atmosphere having a concentration relative to air of about one part

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in a million. Nevertheless, it plays an important role in the maintenance of the observed state of the atmosphere, since it is one of the principal radiatively active constituents. For example, it is ozone that is responsible for the temperature increase with altitude in the stratosphere. Most of the ozone is contained in the lower stratosphere, which effectively acts as a reservoir, but it is produced most efficiently at higher levels between about 45–60 km. Chapman (1930), in one of his brilliant contributions of the 1930's, qualitatively accounted for the formation of ozone as a consequence of the dissociation of molecular oxygen by solar ultraviolet radiation, and the attachment of the resulting atomic oxygen to other oxygen molecules. This is now known as the photochemical theory of ozone; it was first quantitatively investigated by Wulf and Deming (1936), and subsequently by many other workers. Because of the way ozone is formed, theoretically one would expect a latitudinal gradient of the ozone concentrations, with maximum values in the Tropics and minimum values at high latitudes, following from the attenuation of the insolation by the atmosphere. Associated with this would be a seasonal variation with maximum ozone in the summer and minimum in the winter. However, the

first consistent ozone measurements made by Dobson et al. (1927) revealed that the latitudinal gradient of the total ozone amount was the reverse of that predicted photochemically, and also the annual variation exhibited a maximum in spring and a minimum in autumn. This did not lead to the abandonment of the photochemical theory as it had already been realized that the atmospheric motions affected the ozone amount above any one location, but it did emphasize the problem of explaining how these motions brought about the discrepancy with the theory. This gave rise to what has become known as the ozone problem, which is still not entirely resolved today and which represents a problem of considerable scientific interest. Of greater meteorological interest was the realization that since the ozone at low levels in the stratosphere was not in photochemical equilibrium, it became a quasi-conservative property of this region and its movements could be used to deduce atmospheric motions; hence, the concept of using ozone as a tracer arose.

Attempts have been made to deduce directly how the atmosphere maintains its latitudinal ozone concentration gradient by computing the ozone fluxes, and, largely due to the efforts of Newell (1963), it is now known that the maximum ozone amounts at high latitudes are maintained by the transfer of ozone by eddies down the total ozone concentration gradient in the lower stratosphere. Relatively few flux values are available for the Tropics, but the generally northwards fluxes there in the lower stratosphere (Newell, 1963) are weaker than at middle latitudes, which therefore suggests that a direct transfer of ozone from low to high latitudes does not take place. Since ozone is formed most easily at low latitudes, one might have expected the Tropics to act as a direct source for the fluxes at higher latitudes; in addition, the northward transport would also be expected to occur at levels more commensurate with the most efficient production region. The observational studies provide no information as to how the ozone is transported vertically from this region, although the flux calculations of Newell suggest it is at subtropical latitudes. In addition to eddy transport of ozone, there have been suggestions by Brewer (1949) and Dobson (1956) that mean meridional motions could equally well be responsible for the transport of ozone from the tropical source region to the high-latitude reservoir. This is now known as the Dobson-Brewer model, but because of the difficulty of measuring meridional velocities in the atmosphere, relatively little effort has been expended to confirm it.

Theoretical studies of atmospheric ozone have primarily concentrated on the photochemical aspects of the problem, the most widely quoted work in this field being that by Dütsch (1956) and Craig (1950). Improvements in the laboratory data that are required for photochemical calculations have raised some doubt whether the simple oxygen atmosphere originally proposed by Chapman, and normally used in such calculations, is adequate to represent conditions in the actual atmosphere, Hunt (1966a).

Currently, more complex reaction schemes have been proposed (Hampson, 1964), and this particular feature will be discussed later.

Photochemical calculations by themselves will not resolve the ozone problem, and attempts have been made to combine the photochemistry into models that also permit atmospheric motions to transport the ozone. The first such calculation appears to be that by Prabhakara (1963), who used a two-dimensional model in which the eddy transports were parameterized by subjectively chosen eddy diffusion coefficients, and the meridional velocities were arbitrarily chosen. Not surprisingly, he simulated the gross features of the observed ozone distribution; but because of the basic design of the model, little insight was obtained into how the actual atmosphere functioned. A somewhat more realistic approach was adopted by Byron-Scott (1967), who developed a three-dimensional model of the stratosphere based on the NWP grid. He carried out a joint radiative-photochemical-dynamic integration, which was primarily concerned with the sudden warming phenomenon of the winter stratosphere, although he did note that long waves were important for the polewards transport of ozone.

At the present time, the only other numerical investigation related to the ozone problem appears to be that reported by Hunt and Manabe (1968a) in part II of this series of papers. This made use of an 18-level, primitive equation general circulation model, extending from the surface to 4 mb (37.5 km), in which the large-scale diffusion of an idealized ozone like tracer was studied. This tracer was defined initially as a photochemical ozone distribution, but no photochemistry was included in the model; hence, the subsequent changes in the tracer distribution could be unequivocally attributed to transport processes. The analysis of the diffusion of this tracer was most enlightening as regards the insight it provided into the way the atmospheric motions actually transport tracers. The results obtained will not be summarized, but, since they are fundamental to the investigation presented here, part II should be read prior to this paper.

The object of the present study was similar to that of part II, in that starting from an initial photochemical ozone distribution the subsequent three-dimensional diffusion of the ozone by the large-scale motions was followed, only this time allowance was made for photochemical loss and production. Thus, this is a logical extension of the previous work. As a result of this experiment, it was expected that more realistic ozone concentrations would be obtained, as well as more precise information on how the atmosphere maintains its ozone distribution. In particular, information was sought on the extent of the photochemical source region in the stratosphere, as this would indicate where photochemical rather than dynamical control of the O_3 distribution could be expected. In addition, it was hoped to determine exactly how O_3 was transported from the source region to the extratropical lower stratosphere, and what the relative roles of vertical and horizontal

transport by both mean meridional and eddy motions were in this process. Also, since the model was designed so that two tracers could be studied simultaneously, it was decided to investigate two possible photochemical reaction schemes; one was the simple oxygen-only atmosphere generally used, the other was the more complex hydrogen-oxygen atmosphere. In this way it was believed that it might prove possible to delineate between these two basic alternatives and thus clarify the somewhat confusing situation presently existing concerning the photochemistry of ozone. As part of a longer term aim it was hoped that the experiment would also indicate the possibility of a general circulation model calculating its own ozone distribution for use in the radiation calculations, thus removing the need to provide climatological data as at present. This would represent a further step towards making the model more self determining than it is currently, thus permitting joint radiative-photochemical-dynamic studies to be made.

2. INITIAL CONDITIONS AND TIME INTEGRATION

The present model was a direct continuation of the model used in part II; hence, the dynamic and radiative fields were fully developed, being in a state of quasi-equilibrium. This stage corresponded fairly well with early winter conditions in the actual atmosphere, and it has been described in detail in part I, Manabe and Hunt (1968).

The two tracer distributions in the model were re-defined so that their initial conditions corresponded to photochemical equilibrium for their particular reaction schemes. A photochemical reaction scheme was also incorporated for each tracer, and these, of course, endeavored to maintain the photochemical equilibrium conditions in the model atmosphere at all times. These features will be discussed in more detail in section 3. The present model was run for a total of 185 days, the diffusion and photochemical effects being permitted to take place simultaneously throughout this time. The results for the tracer diffusion in part II were based on a diffusion period of 180 days; hence, a direct comparison in time is permitted between the present results and those of part II.

In addition to these changes to the tracers, a modification was made to the vertical momentum exchange mechanism in the model. This was done because the model, as used in part II, was found to have a flaw. This caused the angular momentum of the tropospheric jet to be maintained, to a large extent, from the high-latitude regions, in disagreement with observation. It also resulted in a general equatorward trend, compared with observation, in the position of the major meteorological features in the troposphere; see the discussion by Manabe and Hunt (1968). Although the diffusion of the tracers in the model was apparently unaffected by these discrepancies, the equatorward trend appeared to become progres-

sively worse, and an attempt was made to eradicate the source of this trouble. One of the possible causes was thought to be due to the rather limited way in which the vertical diffusion of momentum was treated in the model. This essentially assumed that the exchange of momentum between the earth and the atmosphere was confined to the model layer adjacent to the earth's surface, which had a depth of 1.65 km. At the suggestion of Dr. S. Manabe this formulation was changed so that, in addition to the surface exchange, each time a convective adjustment was made in the model, owing to the occurrence of a super-adiabatic lapse rate, a vertical momentum exchange also took place between the layers involved in the convective adjustment. For all layers undergoing a convective adjustment, the constant value of $220 \text{ gm cm}^{-1} \text{ sec}^{-1}$ was used for the Austausch coefficient; for nonconvective layers the Austausch coefficient was taken as zero. This value of $220 \text{ gm cm}^{-1} \text{ sec}^{-1}$ is that derived by Palmén (1957) for tropical latitudes, and it is assumed here to be applicable to the convective adjustment procedure used in the model. By relating the momentum mixing and convective adjustment mechanisms, the momentum exchange was confined to the troposphere. In addition, it was most effective at low latitudes where it was hoped that it would destroy a small reverse meridional cell which the model had generated in this region. In practice it was found that the new formulation of the vertical momentum mixing prevented the situation in the troposphere from deteriorating further, but only improved it at a very slow rate, if at all, after an initial improvement. The new formulation was incorporated after the present model had been run for about 80 model days. Note that the zero for all times subsequently referred to is taken as the time at which the present experiment was initiated.

3. PHOTOCHEMISTRY

The two forms of photochemistry considered were treated separately in the model. Since photochemistry can be safely omitted below about 16 km, it was only considered for the top eight levels of the model. Attenuation of the incident solar radiation in the higher atmosphere, above the top level of the model (37.5 km), by ozone and molecular oxygen was included; for simplicity, the total amounts of the gases involved were considered to be invariant with time and latitude.

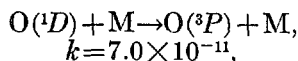
The diurnal variation of the sun was incorporated in the photochemical calculations in the model, although both the dynamic and radiative parts of the general circulation model were restricted to a nondiurnal state, as in part II. This restriction is of little consequence as regards the model dynamics (see Hunt and Manabe, 1968b); hence, the large-scale diffusion of the ozone was unaffected. The diurnal variation is important to the photochemistry, as it limits the time available in which the dynamically produced changes in the ozone distribution can be counteracted photochemically. The solar declination was taken to be

zero for the radiation calculations associated with the photochemistry. This choice was made for ease of computation, despite the fact that dynamically the model was closest to early winter conditions. No allowance was made for Rayleigh scattering in the atmosphere, as the overall accuracy of this study was not considered to be sufficient to justify such a refinement.

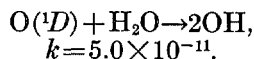
The initial photochemical equilibrium ozone concentrations for both reaction schemes were based on the 1962 U.S. standard atmosphere, and were calculated for the local solar zenith angle for noon in order to obtain the maximum ozone possible at each point. The values of the pressure, temperature, molecular oxygen, and air density required for the photochemical calculations were generated locally as a function of time at each grid point of the model.

Details of the photochemical reaction schemes used here have been given previously by Hunt (1966*b*) and will not be repeated apart from noting some changes made. Both reaction schemes were modified by multiplying the extraterrestrial solar intensities of Tousey (1963) by 0.36, and the molecular oxygen-absorption coefficients of Ditchburn and Young (1962) by 0.75, for the wavelength range 2,000–2,200 Å following the suggestion of Brewer and Wilson (1960). These corrections resulted in a reduction of the photochemical ozone concentrations in the stratosphere. Because of the vital importance of this spectral region to the photochemistry of ozone, it is highly desirable that confirmation of Brewer and Wilson's results should be obtained.

In the case of the oxygen-hydrogen photochemical scheme, several reactions which were of minor concern at stratospheric heights were eliminated. In addition the rate constants of two important reactions were modified, to bring them into better agreement with current estimates. These were the reactions:



and



A constant mass mixing ratio of 3×10^{-6} gm/gm was chosen for the water vapor concentration in the stratosphere for use with this reaction scheme.

As far as the ozone distribution is concerned, the basic difference between the two reaction schemes is that the oxygen-only atmosphere produces unrealistically high ozone concentrations in the stratosphere, whereas the oxygen-hydrogen atmosphere gives more acceptable values, as was first demonstrated by Hampson (1964). However, since the latter reaction scheme must be considered to be unsubstantiated at the present time, it seemed worthwhile to investigate both reaction schemes.

In the general circulation model the diffusion of the O_3 mixing ratio was governed by the following equation,

$$\frac{\partial}{\partial t}(p_*r) = -m^2 \left[\frac{\partial}{\partial X} \left(\frac{p_*Ur}{m} \right) + \frac{\partial}{\partial Y} \left(\frac{p_*Vr}{m} \right) \right] - p_* \frac{\partial}{\partial Q} (\dot{Q}r) + {}_H F_r - p_* C + p_* P$$

where r is the mixing ratio, ${}_H F_r$ the flux divergence of the subgrid-scale horizontal diffusion, C the "precipitation" of the mixing ratio, P the photochemical tendency and p_* the surface pressure. U and V are the velocities corresponding to the X and Y directions, respectively, on the stereographic projection; m is the stereographic map factor; and \dot{Q} is the vertical velocity in the Q coordinate system. Further details concerning the complete system of equations can be obtained from Smagorinsky et al. (1965). Precipitation was arbitrarily imposed by removing immediately any tracer which reached the 16th level (626 mb) or below, the precipitation being accumulated at the surface.

The term of particular interest here is the photochemical tendency of O_3 . For the oxygen-only atmosphere this is governed by the following equations, which can be derived from the conventional reaction scheme:

$$\frac{\partial \text{O}_3}{\partial t} = k_3 \text{OO}_2 \text{M} - k_4 \text{OO}_3 - Q_3 \text{O}_3,$$

$$\frac{\partial \text{O}}{\partial t} = 2Q_2 \text{O}_2 + Q_3 \text{O}_3 - k_3 \text{OO}_2 \text{M} - k_4 \text{OO}_3.$$

Because of computer storage limitations only the O_3 value for each reaction scheme was carried explicitly in the diffusion study. The O value can be obtained uniquely in the lower stratosphere given the values of O_3 , Q_2 , and Q_3 ; hence, the photochemical tendency can be readily obtained in an oxygen-only atmosphere. In the case of the oxygen-hydrogen atmosphere, a knowledge of all the gas concentrations is required. These were obtained by assuming they were in equilibrium with the O_3 concentration, thus permitting their photochemical tendencies to be equated to zero, and using an iterative scheme to obtain the required results. Although various checks indicated that reasonable accuracy was attained for the O_3 photochemical tendency by this approach, it is desirable that in future work all of the gases should be advected individually.

In order to reduce computer time, the photochemical tendency was only evaluated every 12 timesteps (2 hr) and was assumed to remain constant over this period. For the purpose of the photochemical calculations, the atmospheric path length was assumed to vary as the secant of the solar zenith angle, a rather poor approximation for angles greater than 70° , and the solar radiation was arbitrarily cut off at 84° . Unlike an oxygen-only atmosphere, all reactions do not cease after sunset in an oxygen-hydrogen atmosphere, because the OH and HO_2 concentrations decrease rather slowly. Allowance was made for this effect, but its consideration only amounts to the inclusion of a second-order term.

Subsequently, the O_3 distribution for the oxygen-hydrogen atmosphere will be referred to as R3, that for the oxygen-only atmosphere as R4. In part II, R2 was the counterpart of R3 with the photochemistry suppressed in the time integration.

4. LARGE-SCALE DIFFUSION OF R3

Throughout this section a comparison will be made between R2 and R3 in order to illustrate the changes produced by the inclusion of photochemistry for R3.

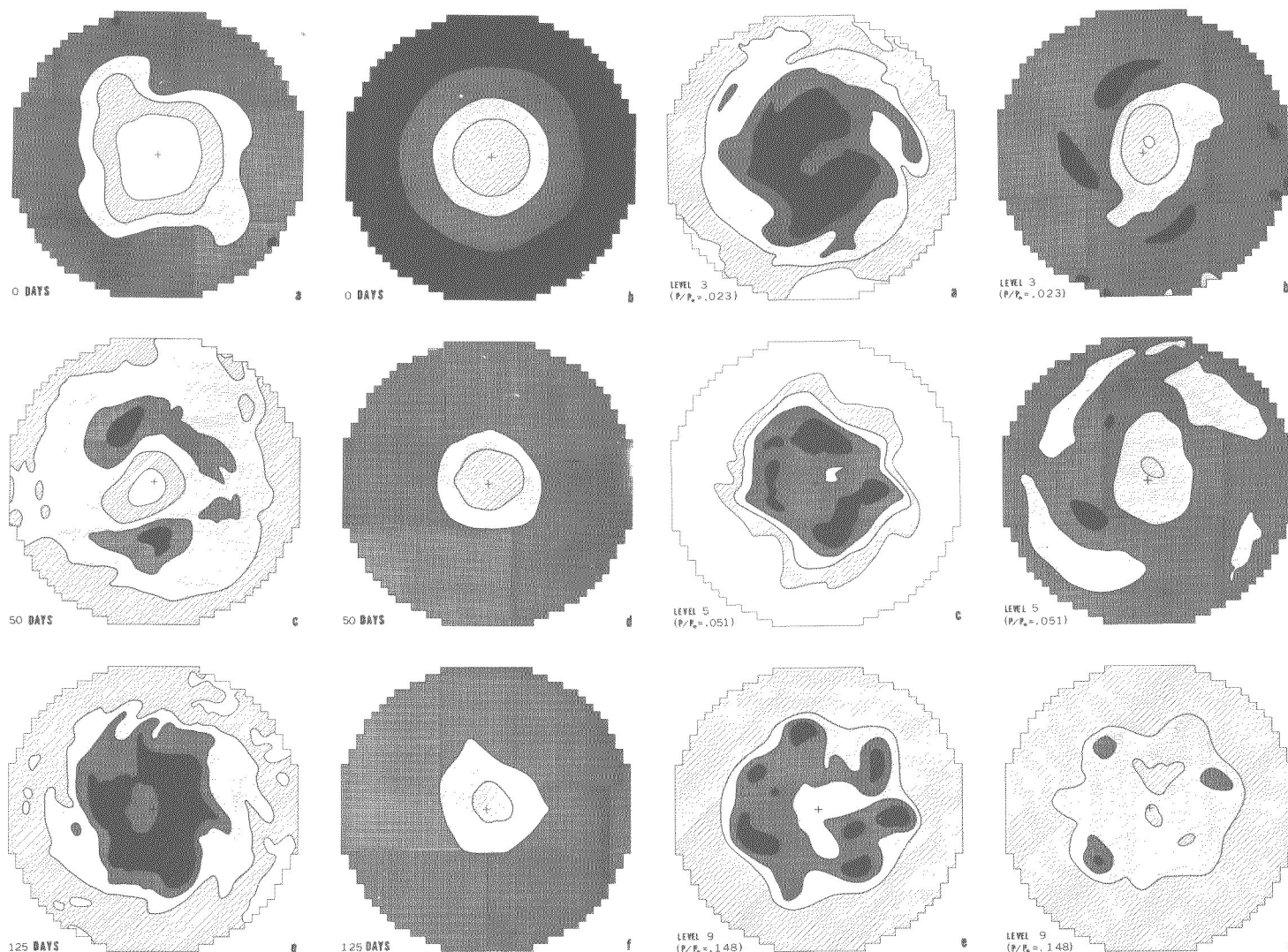


FIGURE 1.—Hemispheric variation of R2 and R3 at level 4 for various instants of time. R2 is on the left, R3 on the right. The color coding used is different for the two tracers. In all cases black is the highest and white the lowest concentration. The cross indicates the position of the Pole.

GENERAL DESCRIPTION

In figure 1, the instantaneous, hemispheric distributions of R2 and R3 are given for level 4 ($p/p_* = 0.036$) of the model for three different times. Because the initial concentrations varied differently with time, the same color coding could not be used for the two tracers in this figure. The contouring selected for R3 was somewhat coarser than that for R2, and thus a direct comparison of the details of the distributions is not possible in figure 1. Compared with the relatively rapid reduction of the tropical R2 concentrations, the corresponding R3 values were fairly stable because the photochemistry attempted to replace the ozone transported to higher latitudes. R2, in general, responded quite differently, as its initial concentration gradient was reversed, and larger concentrations were obtained at higher latitudes than existed initially in the Tropics, owing to downwards transport from levels of higher concentration.

FIGURE 2.—Hemispheric variation of R2 and R3 for various levels 150 days after initiation. R2 is on the left, R3 on the right. The same color coding was used for levels 3 and 5 for both tracers. In all cases black is the highest and white the lowest concentration. The cross indicates the position of the Pole.

Figure 2 compares the R2 and R3 hemispheric distributions for three different levels after diffusion had been acting for 150 days. The same color coding was used in each case, apart from level 9, so that a direct comparison is possible. The dominant feature of the two higher levels shown in figure 2 is that a fairly uniform latitudinal gradient was maintained in the case of R3, in contrast to the marked gradient, particularly in middle latitudes, of R2. Although signs of higher concentrations were beginning to appear in the R3 distributions around middle latitudes, the minimum values remained in the polar regions and the original photochemical latitudinal gradient was still apparent. At level 9, where photochemistry was excluded for both tracers, a similar distribution pattern was apparent; however, the R3 concentrations were generally higher than those of R2 as well as being considerably more uniform.

The difference between the two distributions can be attributed to the photochemistry endeavoring to remove any anomalies in the R3 concentrations which differed from photochemical equilibrium. Since this resulted in smaller concentration gradients, the efficiency of the large-scale eddy transport mechanisms was reduced in the layers where photochemistry was included. It should be noted that the R3 distribution was substantially removed from steady-state conditions in most cases and rather different latitudinal gradients would have been produced by further integration. In particular, the polar minimum would have been removed at the lower levels, and a more extensive buildup in tracer concentration would have been expected in middle and high latitudes. Nevertheless, the two figures leave little doubt that the inclusion of photochemistry substantially influences the diffusion of ozone in the model atmosphere.

LATITUDE-HEIGHT DISTRIBUTION OF R3

The zonally averaged latitude-height distribution of R3 is given in figure 3 for a "doubling" time interval after the R3 initiation. Figure 3a illustrates the basic features of the photochemical distribution, with maximum concentrations at the Equator, minimum at the Pole, and a monotonic decrease in mixing ratio with decreasing height. As a result of the large-scale diffusion, relatively small changes occurred in the R3 distribution over most of the stratosphere. A comparison of figures 3a and 3f shows that R3 has been transported primarily into the lower stratosphere poleward of about 30° lat., this being precisely the change required to bring the photochemical distribution into agreement with observation. The resulting, very uniform latitudinal gradient in the lower stratosphere should be noted, also the contraction of the polar minimum at the higher levels. The crowding of the R3 isopleths around the tropical tropopause and their downwards bulge in the subtropics are features obtained in the R2 distribution, which can be largely attributed to the action of the direct meridional cell at these latitudes as described in part II.

The influence of the photochemistry on the diffusion of O₃ can be seen from figure 4, where the final R2 and R3 distributions are presented. Compared with R3 a quite dramatic reversal of the R2 latitudinal-concentration gradient resulted from the diffusion. Although the dynamical situations were similar, this reversal was not obtained for R3, as the photochemistry not only opposed the dynamically produced accumulation of R3 at high latitudes but also replaced the R3 removed from the Tropics. However, the photochemistry was not able at high latitudes in the middle stratosphere to entirely counteract the dynamical changes, and a slow increase in the R3 occurred there.

The net change produced by the diffusion in the R2 and R3 distributions is shown in figure 5, where the difference between the final and initial concentrations is plotted for the two tracers. The positive region around

30 km at low latitudes in figure 5a was photochemically, not dynamically, produced, as a result of the initial photochemical distribution adjusting to the relatively coarse height structure of the top two levels of the general circulation model. At low latitudes in the middle stratosphere, the R3 concentrations were reduced by about 50 percent less than those for R2, while in the middle stratosphere at high latitudes the R3 increase was considerably less than that for R2 because of the opposition of the photochemistry. The ability of the photochemistry to control the R3 changes in this way can be attributed to the relatively fast photochemical response time of an oxygen-hydrogen atmosphere. This response time is of particular importance in the Tropics, as it ensures that the R3 source region is not depleted by the dynamics, as happened in the case of R2. Some values for the response time are given in the Appendix. In the lower stratosphere and upper troposphere the accumulation of R3 was noticeably faster than that for R2; for example, at level 12 ($p/p_* = 0.284$) there is a factor of 5 difference. The accumulation of tracer at high latitudes at levels below where it was initially defined, as indicated in figure 5, reproduces the atmosphere's use of the lower stratosphere as a reservoir.

As will be shown later, the shaded area of figure 5b corresponds to the photochemical source region of the model atmosphere for equinoctial, solar conditions.

LARGE-SCALE TRANSFER MECHANISMS

Only a rather limited discussion will be given of the transfer mechanisms, as in many details these were similar for both R2 and R3. Figure 6 compares zonal mean latitude-height distributions of the vertical and horizontal fluxes, and the total convergences of R3 for both the mean meridional motions and the large-scale eddies, time-averaged over the last 10-day period of the experiment. Time-averaging is required in order to remove noise from the individual values, which were calculated at intervals of 6 model hours. For some situations, see for example figure 6d, a 10-day period was in fact too short to remove all of the noise. The results shown in figure 6 are, generally speaking, fairly representative of the other 10-day periods, a total of 18 such periods being available from the experiment.

Figure 6a shows that over a large part of the stratosphere R3 was being transferred upwards, i.e., counter-gradient, owing to the vertical flux of the large-scale eddies. The intensity of the downwards flux was noticeably weaker, with this flux being principally concentrated in the region of the tropopause gap. As for R2, very weak downward eddy fluxes existed at most latitudes across the tropopause, but their contribution was very minor compared with the flux through the gap. The principal difference between R2 and R3 on a hemispheric basis is that the high-latitude countergradient vertical eddies, which were confined to polewards of about 70° lat. for R2, have expanded considerably to the detriment of the downwards

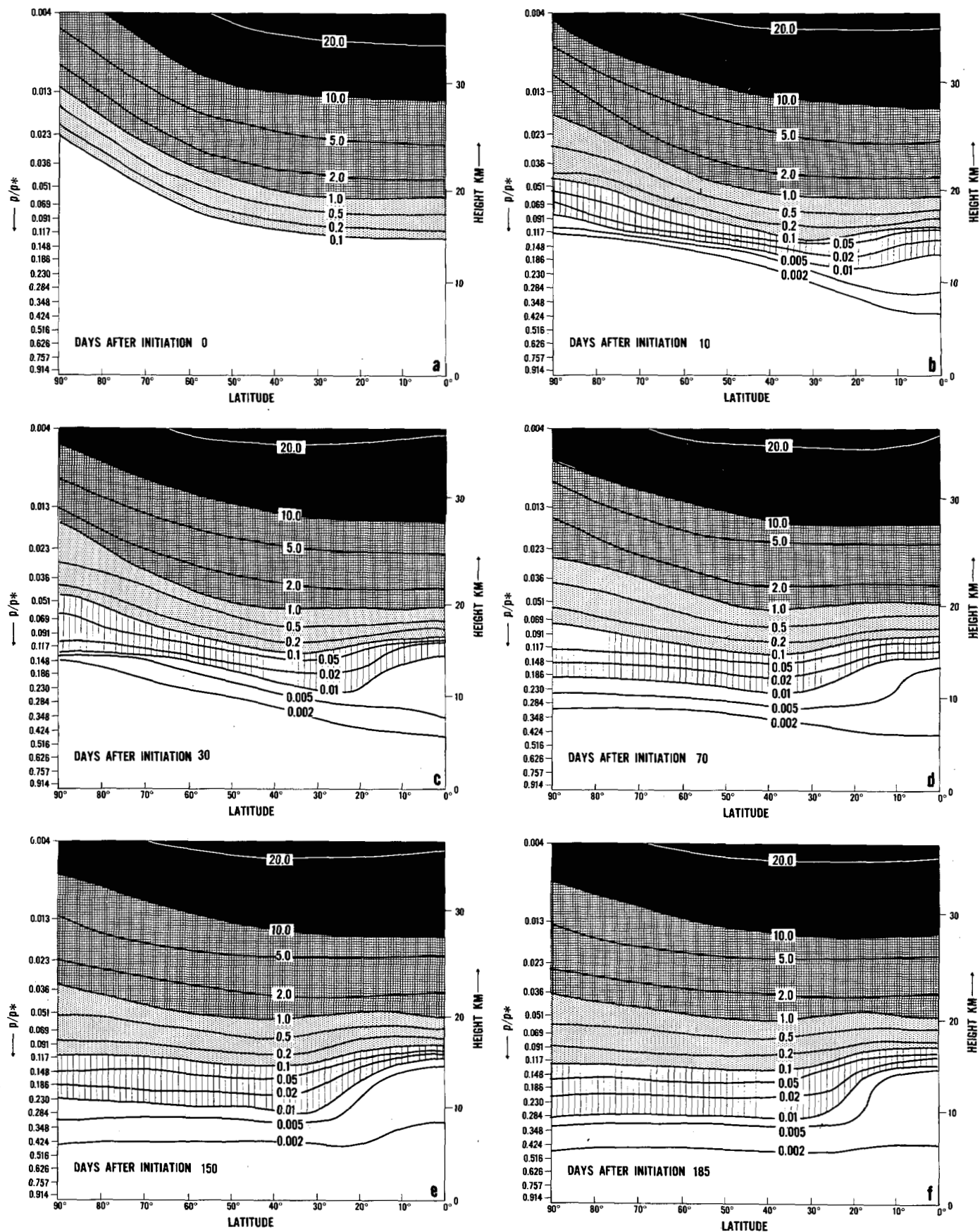


FIGURE 3.—Latitude-height distributions of the zonal-mean R3 concentrations for various times (units: $\mu\text{gm/gm}$).

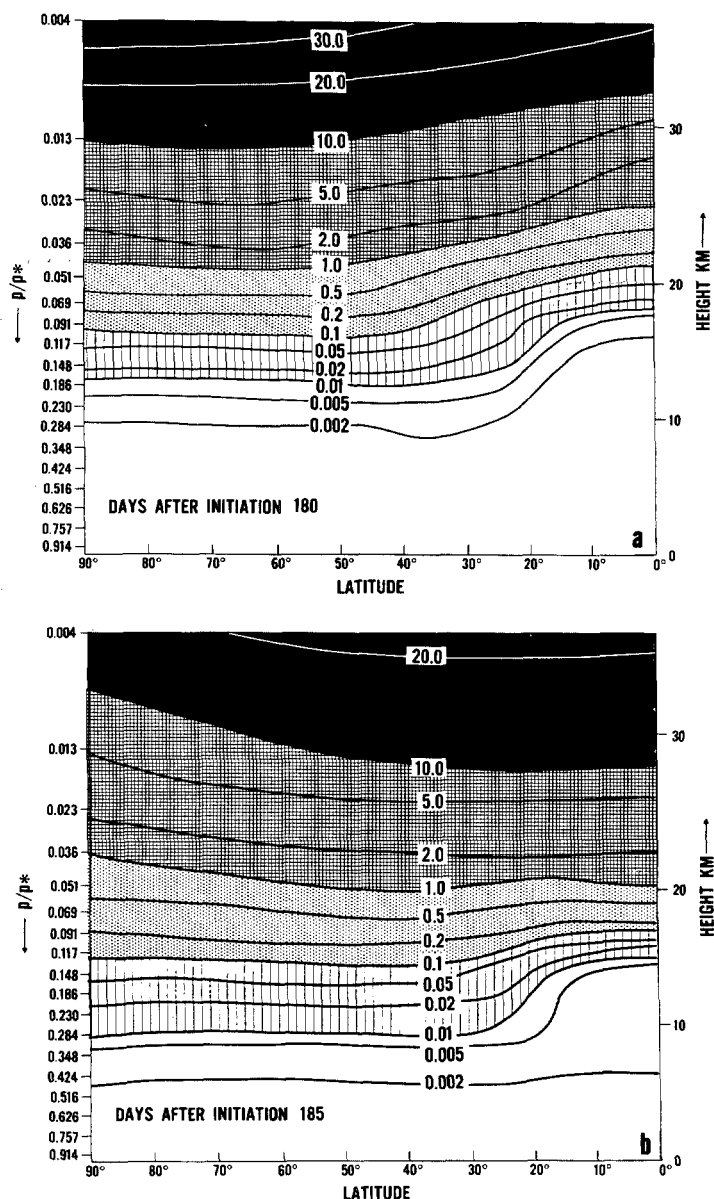


FIGURE 4.—The R2 (no photochemistry) and R3 (with photochemistry) zonal-mean distributions are shown in the upper and lower parts of the figure for conditions at the end of their respective experiments (units: $\mu\text{gm/gm}$).

eddies. This is presumably associated with the existence of the polar minimum in R3 (see fig. 2b) which these eddies were endeavoring to remove.

The vertical flux owing to the mean meridional motions, given in figure 6b, clearly shows the upwards transport in the Tropics and high latitudes, and the associated downward motion in the subtropics, produced by the basic two-cell structure of the model stratosphere. The direct, tropical cell was primarily responsible for the transfer through the tropopause gap, and the fluxes were somewhat larger than those produced by the vertical eddies. The R3 fluxes in figure 6b are not particularly different from the corresponding fluxes of R2, except for a general weakening of the R3 intensities in the strato-

sphere, particularly in the lower stratosphere at high latitudes. The exception to this was the region of the tropopause gap, where the R3 fluxes were noticeably higher than those of R2.

Figure 6c reveals that the horizontal eddy flux reached a maximum in middle latitudes, whereas the maximum might have been expected to be closer to the source region in the Tropics. The fluxes at low latitudes were, in fact, weak and rather variable, and this clearly indicates that a direct eddy transfer from the Tropics to high latitudes is not the way the ozone distribution is maintained. Apart from a general weakening of its fluxes over most of the stratosphere, R3 differed from R2 in that the latter had an extensive region of equatorward horizontal eddy flux at all heights equatorward of about 30° lat. The equatorward horizontal eddy fluxes in the tropical troposphere, shown in figure 6c, supplied tracer from the subtropics in order to compensate for that removed by the upward branch of the direct cell. Since photochemistry is not very efficient at low altitudes it presumably cannot replace the ozone directly, and these fluxes may well be a realistic feature of the actual atmosphere.

The horizontal fluxes produced by the meridional cells, figure 6d, were rather variable, but equatorward of about 35° the fluxes were essentially directed poleward, while at higher latitudes they were in the opposite direction. The maximum intensities were almost invariably in the top level, where the R3 concentrations were largest, and there was a fairly monotonic decrease with decreasing altitude. Although the maximum values of the mean meridional fluxes were greater than those of the horizontal eddies, the efficiency of the mean meridional fluxes was reduced by the appearance of a third meridional cell from time to time at high latitudes, and the eddies were therefore more effective in transporting tracers at these latitudes. The mean meridional fluxes of R2 were somewhat larger than those of R3, but the general distribution pattern was similar. Again the exception to this was in the lower stratosphere in the vicinity of the tropopause where the R3 fluxes predominated.

In figures 6e and 6f the total convergences of the large-scale eddies and the meridional circulations, respectively, are given based on the fluxes shown in the upper part of this figure. Figure 7 shows the breakdown of the eddy convergence into its vertical and horizontal components; such a breakdown is not realistic in the case of the mean meridional motions. Although the convergence due to the horizontal eddies tended to dominate the distribution of the total eddy convergence, the contribution of the vertical eddies amounted to about 20 percent of the total. The net result of the large-scale eddy flux was to remove tracer from low latitudes and to accumulate it at high latitudes, with the biggest loss occurring in the subtropics. The source of the tracer for the subtropics is shown in figure 6f to be the meridional circulations, which accumulate tracer in this region from both the Tropics

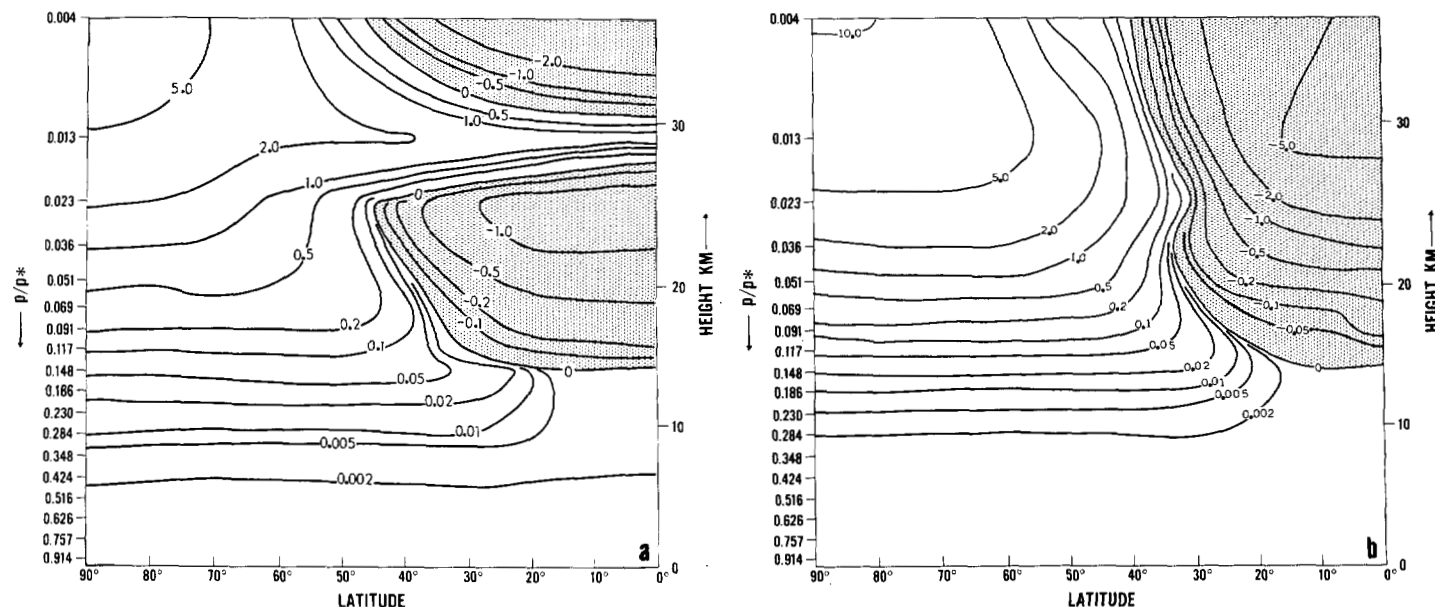


FIGURE 5.—Latitude-height distributions of the difference between the final and initial zonal-mean tracer concentrations, illustrating the changes produced during the course of the experiments. R3 is on the left, R2 on the right (units $\mu\text{gm/gm}$).

and high latitudes. The direct meridional cell at low latitudes is considerably more efficient at removing tracer from the Tropics than the large-scale eddies, and it is this cell rather than the eddies that is considered to initiate the chain of events resulting in the transfer of R3 from low to high latitudes. Polewards of about 20° lat. the meridional and eddy convergences effectively cancel with one another, and this leads to a very slow accumulation of tracer at these latitudes.

A better idea of the differences produced by the inclusion of photochemistry is given in figure 8, where the total convergences of both the eddies and the meridional circulations are compared for R2 and R3. The most obvious difference is that the region of divergence in the eddy distribution is much more limited for R2 than R3. This can be attributed to the R3 removed from the Tropics by the meridional circulation being replaced photochemically rather than by the large-scale eddies, thus permitting an unidirectional flux in the stratosphere. In addition, there has been a general reduction in the maximum intensities of the R3 convergences compared with those of R2, which can be largely attributed to the photochemical dampening. The R3 eddy and mean meridional convergences do not form such an interactive and mutually canceling system as those for R2. A final feature is that the altitudes of the maximum convergences are lower for R3 compared with R2 for both the eddies and meridional circulations, and this tendency is in the direction required to bring the R3 fluxes into agreement with the observed O_3 fluxes.

Subgrid-scale diffusion also contributed to the transport of R2, but since it behaved similarly for both R2 and R3 a latitude-height distribution will not be presented here.

This mechanism is thought to be of secondary importance in the overall diffusion process, as it primarily smoothed out concentration perturbations produced by the large-scale dynamics, rather than acting independently.

The relative roles of the various processes involved in the maintenance of the R3 distribution are illustrated in figure 9, as a function of latitude for two different heights. The photochemical term in this figure is a mean value obtained by integrating over a 24-hr period and is based on the R3 concentrations time averaged over the last 10 days of the experiment. This procedure was not required for the other terms as they did not undergo a diurnal variation. The net rate of change in figure 9 was calculated as the difference between the instantaneous R3 concentrations at the end and beginning of the last 10-day period of the experiment, rather than as a residual. This eliminates errors involved in the computation of the convergences. The various terms in figure 9 do not balance at most latitudes owing to photochemical inaccuracies, truncation errors, particularly in the mean meridional transport, etc.

For level 2 ($p/p^*=0.013$) in figure 9, the mutual opposition of the meridional circulation and large-scale eddies at extratropical latitudes is very apparent. Up to about 30° lat., the photochemistry was replacing the R3 removed from this region by the direct meridional cell, while at higher latitudes the action of the photochemistry was reversed, as it attempted to maintain the photochemical equilibrium R3 value. At the lower height in figure 9, level 8 ($p/p^*=0.117$), the rates of change were more discontinuous owing partially to the presence of a small subsidiary meridional cell at high latitudes (see fig. 6d). However, basically the same

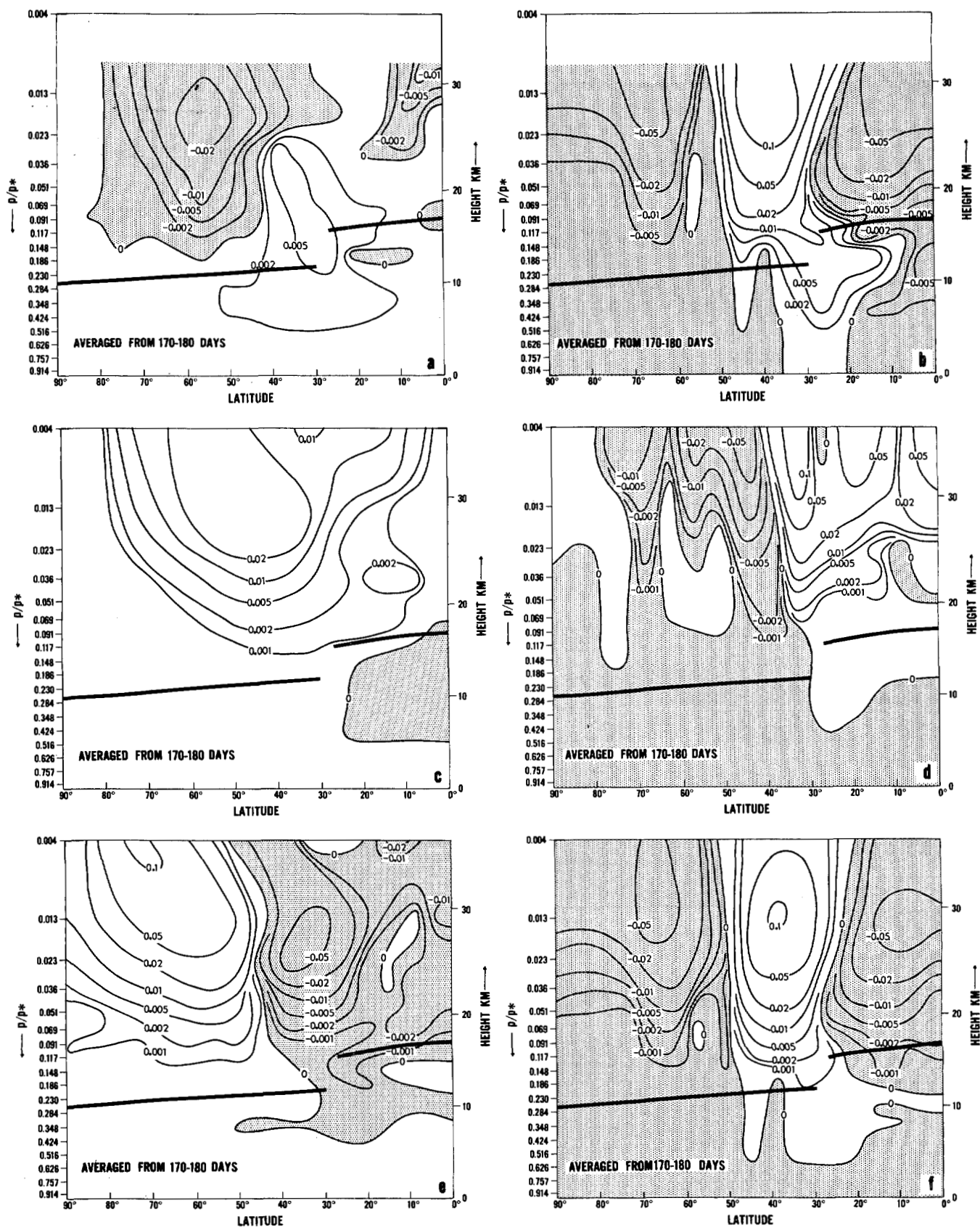


FIGURE 6.—Latitude-height distributions of the R3 fluxes and convergences owing to the large-scale eddies (on the left) and the mean meridional motions (on the right). The vertical fluxes are in the upper part of the figure, shaded areas being regions of upward fluxes (units: $\mu\text{gm}/(\text{cm}^2 \text{ sec}) \times 10^4$). The horizontal fluxes are in the center of the figure, shaded areas being regions of equatorward fluxes (units: $\mu\text{gm}/(\text{atm. sec}) \times 10^{-10}$). The total convergences (combined vertical and horizontal components) are in the lower part of the figure, shaded areas being regions where R3 is decreasing (units: $\mu\text{gm}/(\text{gm sec}) \times 10^5$). The heavy black line indicates the approximate height of the tropopause.

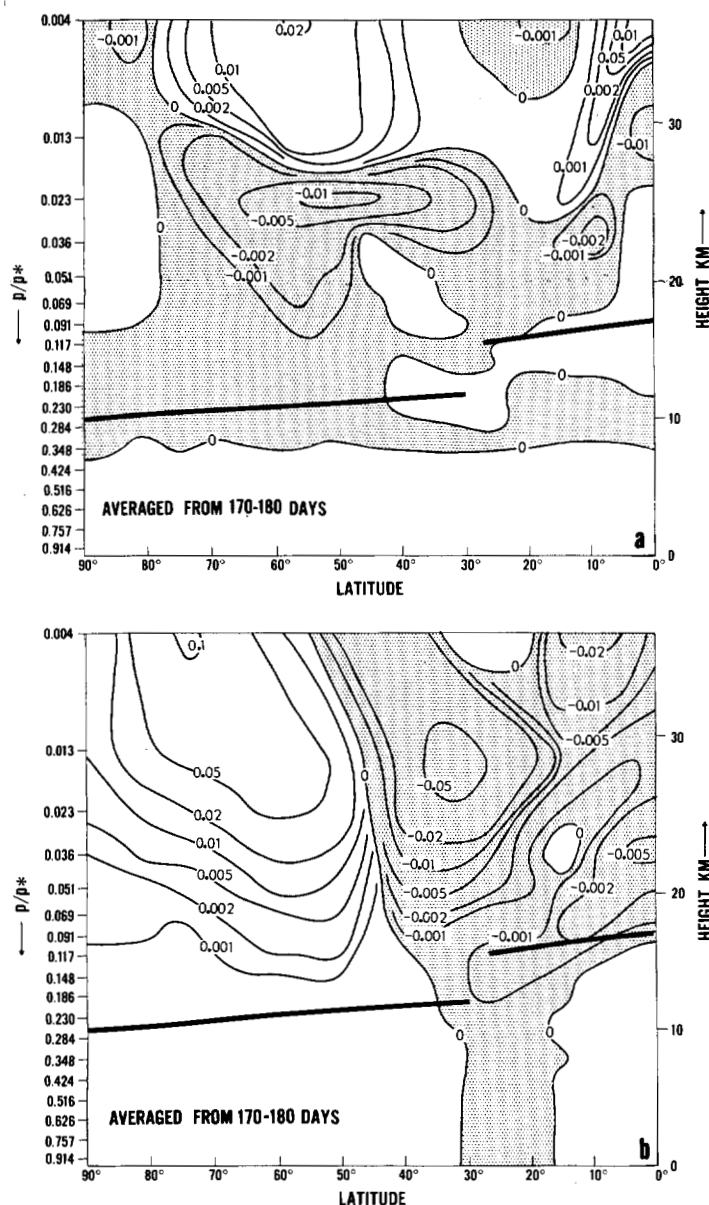
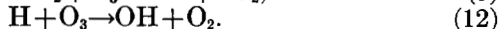
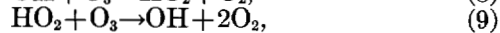
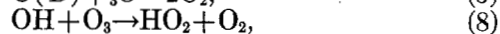


FIGURE 7.—Rate of change of R3 by the vertical (a) and horizontal (b) components of the large-scale eddies. Shaded areas are regions where R3 is decreasing (units: $\mu\text{gm}/(\text{gm sec}) \times 10^5$). The heavy black line indicates the approximate height of the tropopause.

trends existed as in level 2, although the photochemistry was somewhat reduced while the subgrid scale diffusion was more important.

PHOTOCHEMICAL TENDENCY

To conclude section 4, some results will be presented for the various terms in the reaction scheme that are responsible for destroying R3 in the model atmosphere. These terms arise from the following reactions,



These are all terminating reactions in the sense that they result in a net loss of an odd form of oxygen, and it is these reactions which effectively set the level of the photochemical equilibrium O_3 concentrations in the atmosphere.

In figure 10 the vertical distributions of the loss rate for R3 by the above five reactions are presented for noon conditions at 3° lat. These curves are based on the zonal mean R3 values for the last 10-day mean period of the experiment. In an oxygen-only atmosphere, reaction (4) is the only terminating reaction, but it is of secondary importance to the chain reactions (8) and (9), the Hampson mechanism, in an oxygen-hydrogen atmosphere below about 30 km. The virtually identical R3 destruction rates produced by (8) and (9) result from these two reactions constituting an essentially closed regenerating cycle. The destruction of R3 by 12 decreases very fast at the lower levels, as the higher atmospheric densities cause H to be rapidly converted to HO_2 . Reaction (5) is considerably less important than (4), because $\text{O}(^1D)$ is efficiently deactivated to $\text{O}(^3P)$ in the atmosphere. Although not included in figure 10, the destruction of R3 by photodissociation is approximately three orders of magnitude greater than that by either (8) or (9), at all altitudes in the stratosphere. However, photodissociation is not a terminating reaction.

It should be clear from figure 10 why one would expect the R4 concentrations to be considerably larger than those for R3.

5. DISCUSSION OF RESULTS FOR R3

The diffusion of R3 is best considered in terms of the schematic diagram in figure 11. The corresponding diagram for R2 differed from this figure in having eddy fluxes which transported tracer equatorwards from the subtropics at all altitudes, for reasons discussed previously. Also, in the case of R2 there was no photochemical source region. Although the general details and explanation of the diffusion are similar for both R2 and R3, for completeness, an abbreviated explanation will be given in order to emphasize the interaction of the photochemistry and the dynamics.

Figure 11 shows that R3 was transported by the direct meridional cell from the tropical source region to the subtropics, producing the M^+ region there. Owing to the variation of the R3 concentration gradient with height, the vertical, rather than the horizontal, component of this cell was primarily responsible for this M^+ region. Because of the photochemical replenishment of the R3 removed by the dynamics from low latitudes, a poleward large-scale eddy flux from the Tropics was permitted, but this was rather ineffective compared to the mean meridional flux, as the dampening action of the photochemistry resulted in small R3 latitudinal-concentration gradients at low latitudes. If the large-scale eddies acted alone, one would expect a much slower diffusion. A further consequence of the photochemistry was that the tropical source

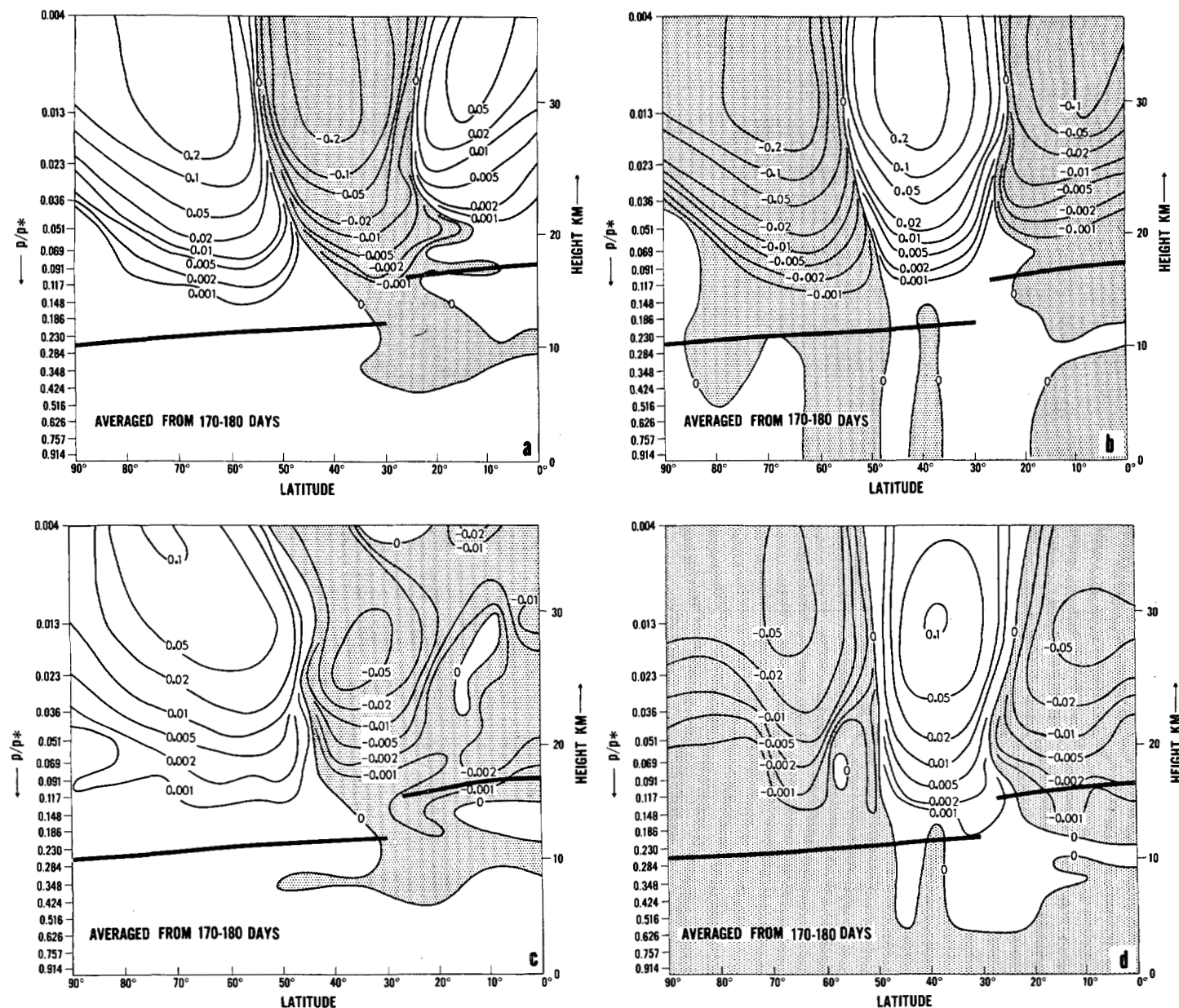


FIGURE 8.—The total convergences for R2 are given in the upper part of the figure, those for R3 in the lower part. Eddies are on the left, the mean meridional motions on the right. Shaded areas are regions where the concentrations are decreasing (units: $\mu\text{gm}/(\text{gm sec}) \times 10^5$). The heavy black line indicates the approximate height of the tropopause.

region was maintained at a fairly constant level, which resulted in more tracer being transported to lower altitudes in the subtropics than in the case of R2, whose concentrations at low latitudes decreased continuously. Hence, compared with R2, the R3 M^+ region in the subtropics acted as a more efficient source for the high latitudes, particularly in the lower stratosphere. The tracer from the M^+ region in the subtropics was transported primarily by the large-scale eddies quasi-horizontally to higher latitudes, producing the E^+ regions there. The accumulation of tracer at these latitudes was opposed by the indirect meridional cell in that region. This cell, owing to the associated vertical and latitudinal concentration gradients of the tracer, produced divergence from the

high latitudes and convergence in the subtropics, thus reinforcing the action of the direct cell in that region. Photochemistry also opposed this accumulation of the tracer, but it was not effective enough at these latitudes, particularly in the lower stratosphere, to be able to greatly influence the tracer concentrations.

The reason why this large-scale diffusion mechanism results in an accumulation of tracer in the lower stratosphere at extratropical latitudes has been discussed in part II. Briefly the explanation is that although the indirect meridional cell opposes the action of the eddies, it effectively only cycles the tracer around, thus conserving it, and this combined with the continual fresh supply from the Tropics leads to a net accumulation. To complete this

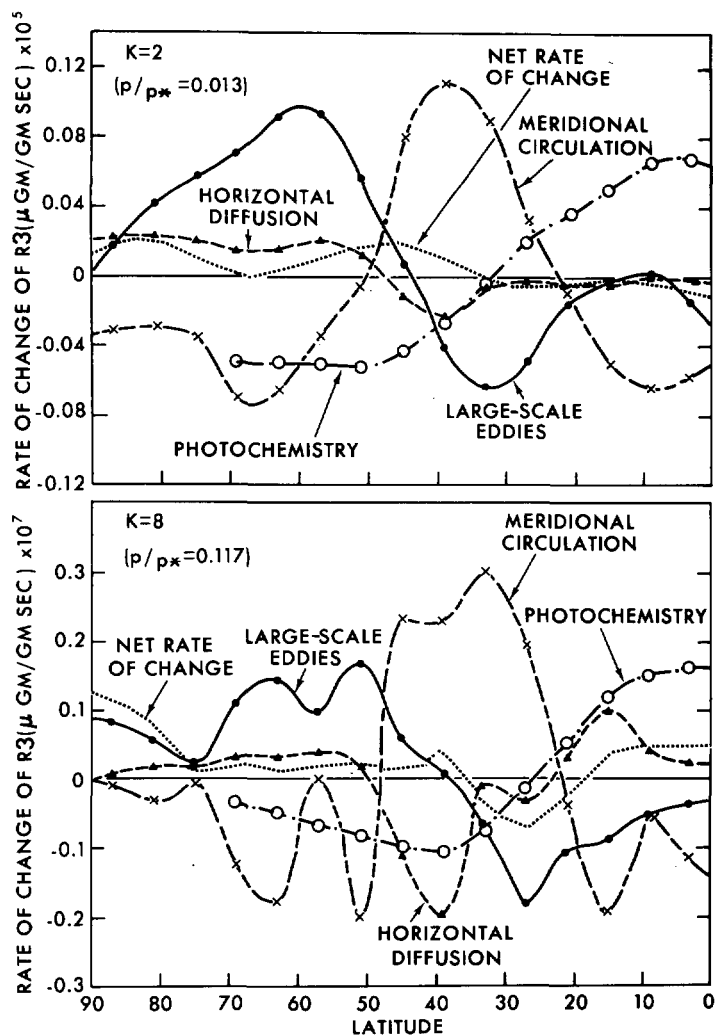


FIGURE 9.—Rate of change of R3 versus latitude for the various mechanisms, averaged over the last 10 days of the experiment. Results are shown for levels 2 and 8.

explanation it is also necessary to explain why the tracer is transported mainly poleward by the eddies in the lower stratosphere, rather than equatorward where the horizontal concentration gradient is directed (see fig. 3f). This feature has also been discussed in part II in connection with the diffusion of R1. The explanation requires an analysis of the synoptic situation associated with the upper level trough and ridge pattern in the stratosphere. This was not done for R3, as there was no reason to expect it to behave differently to R1 in this respect. The R1 synoptic analysis revealed that, because the downwards motion over a trough corresponds with poleward motion, this will lead to a transfer of tracer-rich air towards higher latitudes owing to the vertical concentration gradient of R3. On the other hand, for a ridge in the lower stratosphere the corresponding air motions are directed upwards and equatorwards, which will lead to tracer-poor air being transported towards the Tropics, again because of the vertical gradient of R3. The result is that there is a net transfer of

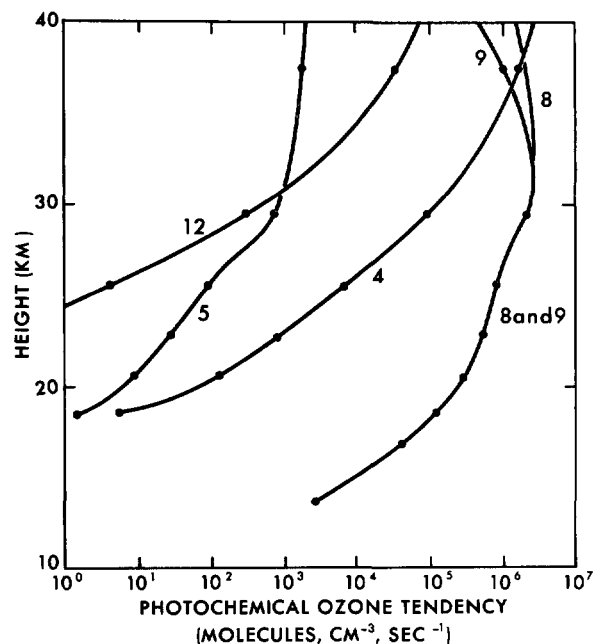


FIGURE 10.—The rate of loss of R3 owing to various reactions is illustrated as a function of height for conditions at noon in the Tropics. The numbers on the curves refer to the reactions in section 4, Photochemical Tendency.

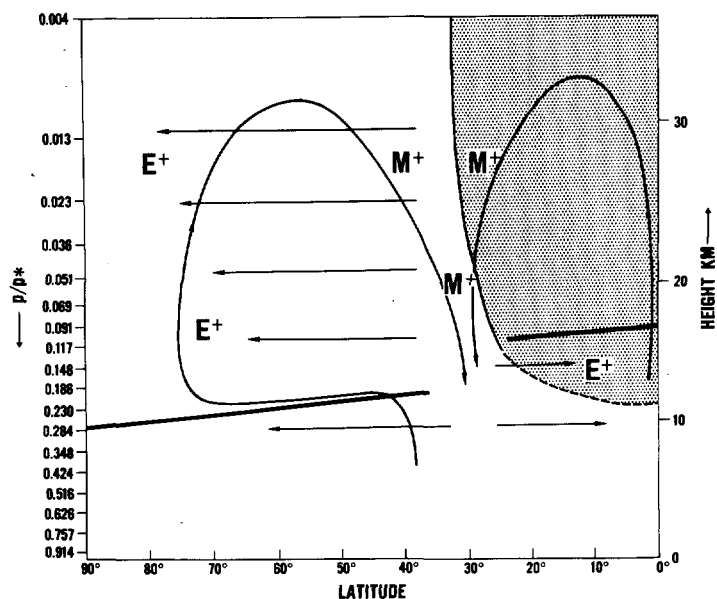


FIGURE 11.—Schematic diagram showing the combined actions of the large-scale eddies and the meridional circulation for quasi-steady conditions for R3. E^+ and M^+ represent regions of convergence by the eddies and meridional circulation, respectively. The horizontal arrows indicate the regions where the eddies are primarily active, and the shaded area roughly corresponds to the photochemical source region in the model.

R3 into the lower stratosphere at extratropical latitudes, which can be attributed to the large-scale eddies.

Although the R3 concentrations in the lower stratosphere obtained from the present experiment were con-

siderably smaller than the O_3 concentrations in the actual atmosphere, the above description is thought to be of general validity for winter conditions. Some aspects, such as the predominance of the vertical countergradient eddies in the middle stratosphere at high latitudes (see fig. 6a) would be expected to be reduced as the R3 concentrations increased in that region. The existence of such countergradient eddies can be understood when they are combined with their horizontal components and superposed on the latitude-height distribution of the tracer. As demonstrated in part II, the total eddy vector is always directed down the tracer-concentration gradient. Other more minor aspects, such as the reason for the discontinuity in the vertical distribution of the tracer at the tropopause, and the low tropospheric tracer concentrations, have been explained in part II and will not be repeated here.

It will be readily appreciated that the above description of the large-scale diffusion of R3 is not intuitively obvious from the variation with time of the latitude-height distribution of R3. Probably the single most important feature in the transfer of R3 from the tropical source region to the reservoir in the lower stratosphere at higher latitudes is the downwards motion in the subtropics associated with the direct meridional cell.

6. COMPARISON OF R3 WITH OBSERVATION

The zonal mean latitude-height distribution of R3 for the last day of the experiment is compared in figure 12 with an annual mean O_3 distribution given by Hering and Borden (1965), which is based on the North American ozonesonde network. Ideally, a more representative zonal mean O_3 distribution would have been preferred, obtained by means of an absolute O_3 measuring sonde rather than the chemiluminescent sonde used by Hering and Borden. In the subsequent comparison these limitations of the observational network should be borne in mind.

Qualitatively, there are regions of broad agreement between the R3 and O_3 distributions, despite the premature termination of the experiment. Thus, both tracers have a similar tendency for their concentrations to be invariant with latitude, for a given height, in the lower stratosphere and upper troposphere polewards of about 35° lat., and for their isopleths to rise in the region of the tropical tropopause. Although insufficient observations were available for a detailed comparison in the middle stratosphere it appears that the R3 concentrations are too high, presumably owing to the choice of some terms in the photochemical equations. More observations are required at the upper levels, particularly at high latitudes. The agreement between the R3 and O_3 concentrations in the Tropics is considerably better than for R2 and O_3 (fig. 29, part II), because of the photochemical replenishment. However, the R3 isopleths are noticeably more crowded than those of O_3 and rise more rapidly in the region of the tropical tropopause, probably indicating

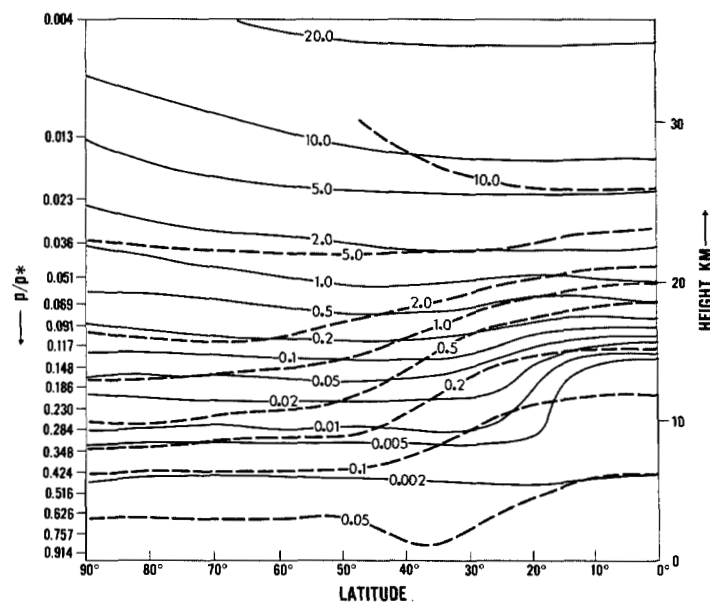


FIGURE 12.—Comparison of the zonal-mean R3 distribution at 185 days with an annual mean O_3 distribution (dashed lines) based on the North American ozonesonde network (units: $\mu\text{gm/gm}$).

that the upwards branch of the tropical meridional cell is too intense in the model. The largest discrepancy is in the values of adjacent R3 and O_3 isopleths below about 20 km, for example at level 10 ($p/p_* = 0.186$) the O_3 concentration is higher by a factor of about 10, depending on latitude, and by an even larger factor at lower levels. Continued integration would have resulted in better agreement at these levels, but the computer requirements were too excessive to attempt to achieve an equilibrium state by this approach.

In figure 13, initial and final R3 profiles for three latitudes are compared with representative O_3 profiles measured by Hering and Borden (1964). The final R3 profiles are instantaneous local values and should therefore be directly comparable with the observed data. The concentrations in the figure are given in terms of molecules/cc, since the use of ozonograms in such a comparison produces a rather distorted picture. The agreement with observation was best in the Tropics, but even there the dynamics were able to prevent photochemical equilibrium from being maintained between 15 and 20 km. At lower levels the R3 concentrations were considerably below those for O_3 , although both tracers behaved similarly in having discontinuities in their profiles somewhat below their respective tropopauses. Relatively minor changes occurred in the R3 concentrations in the subtropics during the course of the experiment, apart from transport of tracer down to lower levels. Below about 25 km, the R3 values were considerably less than those of O_3 , and it is not clear whether further integration would have improved this situation. The secondary peak in the O_3 profile at 12 km is a fairly common feature in this region and is thought to be related to intrusions of polar air through

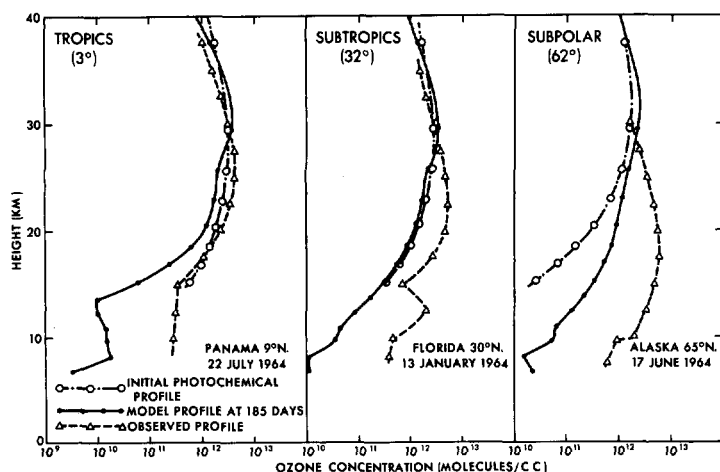


FIGURE 13.—Comparison of the initial and final R3 profiles at selected latitudes with representative ozonesonde profiles.

the tropopause gap. The model resolution is probably too coarse to permit such features to be obtained in the present experiment. At higher latitudes an increase in the R3 concentrations occurred at all levels, with particularly substantial increases at the lower levels. Despite this, the R3 concentrations were well below those of O_3 in the lower stratosphere, though a considerable improvement would have been expected from a more extended study. Again, both tracers had discontinuities in their vertical concentration gradients in the region of the tropopause.

In figure 14, observed and computed total ozone amounts are compared as a function of latitude. At all latitudes the R3 amounts were considerably less than the observed amounts, although a significant increase had occurred in the polar regions. Obviously, a substantial transfer of R3 into the lower stratosphere reservoir is needed to improve the agreement. The decrease in the total R3 amount at low latitudes can probably be largely attributed to the direct tropical cell's being somewhat too strong in the model.

Relatively little information is available as regards observational data on the atmospheric transport mechanisms. Newell (1963) found that for most of the year in the Northern Hemisphere there were generally polewards, transient-eddy fluxes at all latitudes at 50 and 100 mb. Equatorward of about 30° lat. these fluxes were approximately one-third of those from 30° – 60° , which suggests that the downwards fluxes obtained in the model around 30° (see figs. 6a, b) are the source of the additional tracer for the midlatitude fluxes. The latitudinal variation of the horizontal R3 eddy fluxes in figure 6c is considered to be in satisfactory agreement with Newell's findings, although much more extensive observations are required to substantiate the model. Hering (1966) has presented more accurate transient eddy fluxes for O_3 for midlatitudes based on the North American ozonesonde network. He also found a poleward flux at all seasons, but, rather sur-

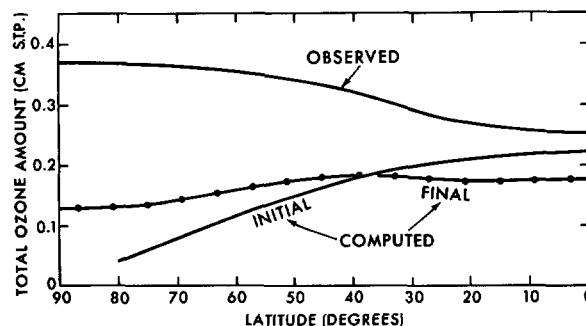


FIGURE 14.—The variation with latitude of the total R3 amount in a vertical column of the atmosphere, for initial and final conditions, is compared with the observed total ozone amount for annual mean conditions given by London (1962).

prisingly, the fluxes were limited to between the tropopause and 18 km. In the model the maximum polewards flux over midlatitudes was at about 30 km, and significant fluxes were obtained at all heights in the stratosphere at these latitudes. The R3 fluxes were in better agreement with observation than those for R2, and continued integration might have produced a further improvement. However, it should be noted that Hering based his flux values on O_3 concentrations expressed in $\mu g/m^3$, whereas $\mu g/g$ were used here. When the fluxes in figure 6c are converted to the same units as used by Hering, the height of the maximum flux is reduced to about 25 km, and a better overall agreement is obtained.

No direct information on vertical O_3 transport in the atmosphere appears to be available. As discussed in part II, some radioactive tracers in the stratosphere imply upwards transport in the Tropics and downwards transport in the subtropics, and these motions are considered to indicate the existence of a tropical meridional cell at these heights. Thus, some support is provided for the very vital function assigned to this cell in the model.

No results will be presented for synoptic features as these have been adequately dealt with in part II, where it was shown that good agreement with observation was obtained.

7. LARGE-SCALE DIFFUSION OF R4

The results for R4, the O_3 mixing ratio based on photochemistry in an oxygen-only atmosphere, will be presented very briefly in this section. This is possible because in most ways R4 behaved similarly to R3 following the close correspondence of their vertical and latitudinal concentration gradients.

MODEL RESULTS

In figure 15 the instantaneous, zonally averaged, latitude-height distribution of R4 is illustrated for the initial and final conditions. Compared with R3, the initial R4 concentrations were rather high at all latitudes, although the photochemical trend is very apparent. The

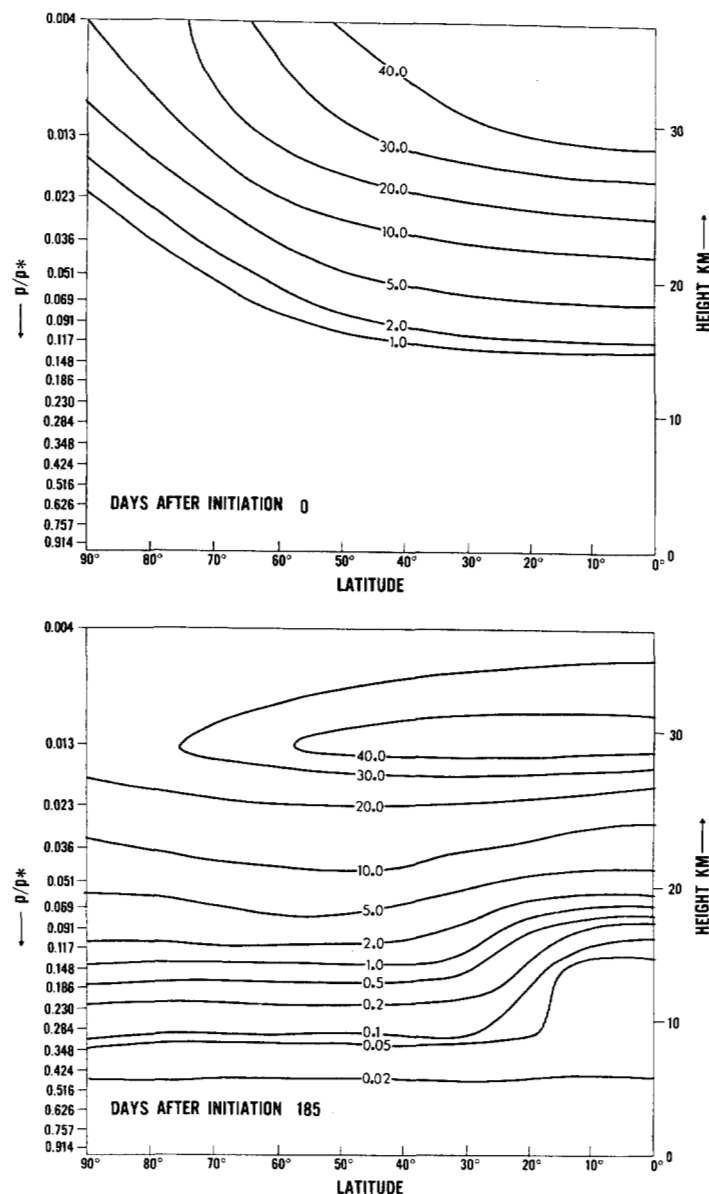


FIGURE 15.—Latitude-height distributions of the zonal mean R4 concentrations for initial and final conditions (units: $\mu\text{gm/gm}$).

adjustment of this photochemical distribution to the height structure of the general circulation model was even more noticeable than for R3, and, as a result, the final R4 mixing ratio shown in figure 15b had a clear maximum at about 30 km. This result arose from photochemical rather than dynamical effects and is an artificial feature of the model. Apart from this feature the development of the R4 distribution followed a pattern close to that of R3, with a general accumulation of tracer at high latitudes, particularly in the lower stratosphere. The invariance of the mixing ratio with latitude at extratropical latitudes and the rise of the isopleths in the region of the tropical tropopause reproduce trends familiar from the R3 distribution.

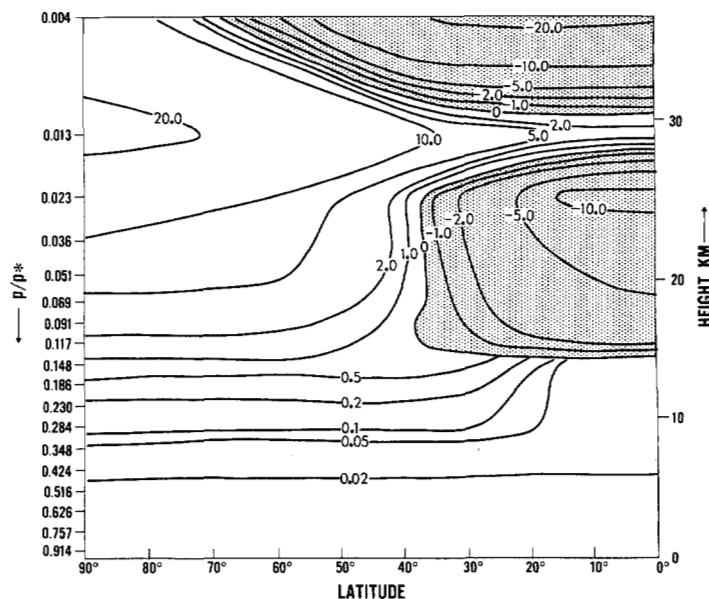


FIGURE 16.—Latitude-height distribution of the difference between the final and initial zonal mean R4 concentrations, illustrating the changes produced during the course of the experiment (units: $\mu\text{gm/gm}$).

The net result of the large-scale diffusion of R4 is shown in figure 16, where the difference between its zonally averaged final and initial distributions is presented. The overall pattern is similar to that for R3 in figure 5a, the positive region around 30 km in the Tropics being caused by the initial photochemical adjustment mentioned above. Much larger changes occurred in the R4 distribution than that for R3, particularly in the middle stratosphere. However, the largest percentage increase was in the "reservoir" in the lower stratosphere at extratropical latitudes, where the final R4 concentrations attained values 10 times as great as those for R3. Generally, the initial, high concentrations in the Tropics were considerably reduced by the dynamics (and by the initial photochemical adjustment), and this is precisely what is required to obtain agreement with observation at these latitudes. The fact that these reductions were much larger than for R3 illustrates the much slower, photochemical response times that are obtained with an oxygen-only atmosphere (see Appendix). As a consequence, such an atmosphere is a less efficient photochemical source for O_3 than the corresponding hydrogen-oxygen atmosphere. Hence, unlike the situation for R3, the oxygen-only atmosphere is incapable of entirely replenishing by photochemical means the O_3 removed by the large-scale dynamics from the source region in the Tropics. This reveals that the many oxygen-only photochemical O_3 distributions that have been calculated for equatorial conditions and which were found to be in reasonable agreement with observation would be expected to be unsatisfactory once large-scale dynamic effects were incorporated.

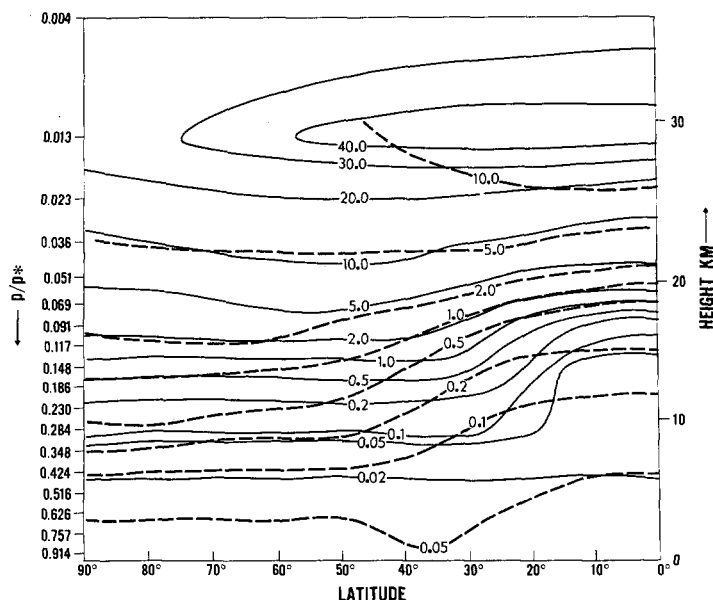


FIGURE 17.—Comparison of the zonal-mean R4 distribution at 185 days with an annual mean ozone distribution (dashed lines) based on the North American ozonesonde network (units: $\mu\text{gm/gm}$).

Regarding the large-scale transfer mechanisms, no figures will be presented for these since they add very little to those given previously for R3 in figure 6. Generally, the R4 fluxes and convergences, both eddy and mean meridional, were approximately twice those of R3 in maximum intensity and also extended to lower altitudes. In the case of the horizontal component of the large-scale eddies, equatorward fluxes occurred somewhat more frequently than for R3 in the Tropics at about level 3 ($p/p_* = 0.023$), but they were less than one-tenth of the intensity of the usual poleward fluxes in this region. The other principal difference was that these eddy fluxes and also the total convergences of both the large-scale eddies and the meridional circulations had maximum values at level 3 rather than level 2, as was the case for R3.

The explanation of the diffusion of R4 is obviously identical with that given for R3 and need not be repeated here. The schematic figure illustrating the diffusion of R3 (fig. 11), therefore, also applies to R4.

COMPARISON WITH OBSERVATION FOR R4

In figure 17 the zonally averaged latitude-height distribution of R4 for the last day of the experiment is compared with the Hering-Borden ozonesonde results. The same basic similarities exist between the two distributions as in the case of R3. However, in the middle stratosphere the R4 concentrations are considerably higher than observed at all latitudes, while in the lower stratosphere and upper troposphere there has been a noticeable improvement in the agreement with observation compared with R3. Even at the lowest levels the R4 concentrations are within roughly a factor of 2 of observa-

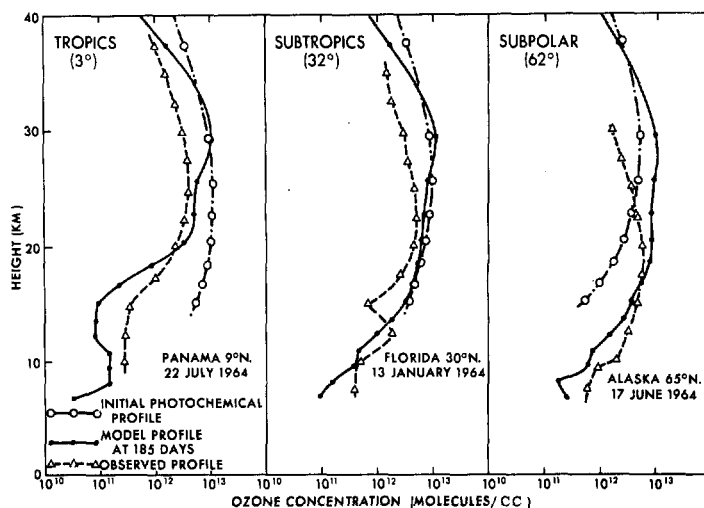


FIGURE 18.—Comparison of the initial and final R4 profiles at selected latitudes with representative ozonesonde profiles.

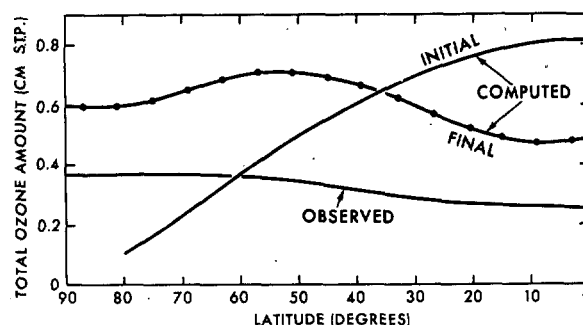


FIGURE 19.—The variation with latitude of the total R4 amount in a vertical column of the atmosphere, for initial and final conditions, is compared with the observed total ozone amount for annual mean conditions given by London (1962).

tion, although the R4 isopleths still rise too fast in the Tropics. A more detailed comparison of individual O_3 and R4 profiles is given in figure 18, and this shows that changes similar to those for R3 in figure 13 were produced in the R4 distribution during the experiment. In the Tropics, only below 20 km was R4 less than O_3 , and this is attributed to the tropical meridional cell in the model being too strong. In the subtropics R4 exceeded O_3 at virtually all heights, and even at high latitudes the R4 concentrations were approaching those of O_3 at low levels. Since the R4 concentrations in the lower stratosphere reservoir were still increasing steadily when the experiment was terminated, it is premature to assume a steady state had been obtained in the model. Therefore, the situation shown in figure 18 is unlikely to be improved by further integration, and this suggests that photochemistry in an oxygen-only atmosphere, at least as formulated here, is not applicable to the actual atmosphere.

In figure 19 the computed, initial and final, R4 total amounts are compared with the observed total O_3 amount. Although the final computed values are in better agree-

ment with observation, they are between 50 and 100 percent higher than the O_3 values, and thus clearly demonstrate the failure of the R4 reaction scheme.

8. CONCLUDING REMARKS

It has been demonstrated that, starting from a photochemical O_3 distribution, the dynamic and photochemical processes in the model produce an O_3 distribution which is qualitatively in agreement with observation. Since the experiment was not continued until either of the tracer distributions had attained a steady state, only somewhat qualified conclusions can be drawn from the results. Nevertheless, it is thought that the large-scale transfer mechanisms, as summarized in figure 11, probably represent the transport processes which exist in the spring and winter in the actual atmosphere. The poleward transport of O_3 is initiated by the action of the direct meridional cell in the Tropics, which supplies O_3 to the subtropics. The large-scale eddies continue this poleward transport by removing quasi-horizontally the O_3 deposited in the subtropics, the mechanism by which the eddies effect this being governed by the trough and ridge pattern in the lower stratosphere. The essential function of the photochemistry was to replace the O_3 removed from the Tropics, and since this damped the horizontal O_3 concentration gradients at low latitudes, it severely restricted the direct transfer of O_3 by the large-scale eddies from this region. At high latitudes the photochemistry opposed the dynamically produced accumulation of O_3 , but was unable to prevent it.

The model results show that, even allowing for dynamical effects, photochemistry in an oxygen-only atmosphere still produces O_3 amounts in excess of those observed at most locations. Hence, unless the rate constants used here are substantially in error, or the solar radiation intensities in the ultraviolet incorrect, it appears unlikely that this photochemical reaction scheme is representative of the situation existing in the actual atmosphere. Also, in view of the slow, photochemical response times of this reaction scheme, it may not be possible to supply sufficient O_3 to account for the spring maximum in the total O_3 amount. On the other hand, the oxygen-hydrogen atmosphere photochemistry produced O_3 concentrations, which, in general, were below those of the actual atmosphere. It appears likely that extended integration of the model would have resulted in better agreement, particularly at the lower levels, but it is not possible to assess fully the applicability of this reaction scheme to the actual atmosphere at the present time. In view of the uncertainty of many of the rate constants required, there is a high probability that future laboratory experiments may result in substantial changes to this reaction scheme. Since the oxygen-hydrogen atmosphere is a considerably more efficient photochemical source than the oxygen-only atmosphere, it should be able to cope with the O_3 requirements associated with the spring maximum.

In general, the computed results were in substantial agreement with observation, particularly regarding the limited observational information available on the transport mechanisms. However, the present study provides no information concerning how the seasonal variations in the O_3 amounts occur. It seems possible that the transport mechanism of the present model prevails throughout the spring buildup in the O_3 , and that this occurs because of a rise in the meteorological activity in the lower stratosphere produced by an increase in the upward flux of energy from the troposphere, as suggested by Newell (1964). The decrease in the O_3 concentration in the summer and autumn may be associated with a different type of mean meridional circulation pattern, or perhaps just much weaker transport mechanisms than those existing in the present model. Further experiments are required to clarify this point.

9. APPENDIX

PHOTOCHEMICAL RESPONSE TIME OF OZONE

It is well known that ozone is generally considered to be a conservative property of the atmosphere below about 35 km, where it is no longer in photochemical equilibrium. This departure from equilibrium occurs because the ozone at these heights is protected from the sun's ultraviolet radiation by the ozone above; hence, greater than equilibrium concentrations can be accumulated by the atmospheric motions. An approximate estimate of the time required for the photochemistry to restore photochemical equilibrium concentrations, assuming all atmospheric motions had ceased, is obtained from the so-called half restoration time (Craig, 1950; Dütsch, 1956). This is the time required for a perturbation from the equilibrium concentrations to be changed by e^{-1} ($e=2.718$).

Results for the half-restoration times in an oxygen-only atmosphere have been presented by a number of authors, and although quantitatively these have differed considerably owing to the use of different rate constants, etc., qualitatively they all give the same variation with altitude. Thus, above 40 km, times of the order of hours or less are obtained, which indicate that photochemical equilibrium should be maintained. At lower altitudes, the half-restoration times increase monotonically with decreasing height, and times of the order of months or years are predicted at 25 km.

The photochemical response of the atmosphere was investigated for both of the reaction schemes incorporated in this experiment, by means of an approach suggested by Dr. S. Manabe. This consisted of simultaneously integrating the photochemical equations for each reaction scheme, starting from initial conditions of zero concentrations for all constituents. The 1962 U.S. standard atmosphere was used in this study, and the solar zenith angle was maintained constant through the integration. The complete reaction scheme of Hunt (1966b) was used,

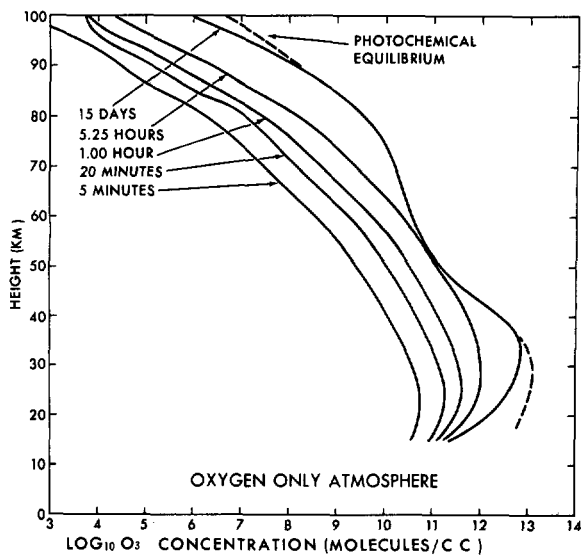


FIGURE 20.—Photochemical growth curves of the ozone concentrations for an oxygen-only atmosphere illustrating the approach to photochemical equilibrium.

and the Brewer-Wilson corrections to the solar intensity and the oxygen absorption coefficients were omitted. The photochemical equations were integrated by a partially implicit method which incorporated an iteration procedure in order to improve the accuracy. These response calculations were made for the altitude range 98–16 km at intervals of 2 km.

An advantage of the method used here is that the O_3 and other gas concentrations are consistently related at all times, unlike the situation with the usual method of calculating half-restoration times. The growth of the gas concentrations with time can also be followed, and information is therefore provided on the absolute times required to attain photochemical equilibrium. It is also possible to study directly an arbitrary perturbation made to the photochemical equilibrium O_3 concentrations at any given altitude. The principal disadvantages of the method are its relative complexity and the amount of computer time required.

The growth curves for O_3 in an oxygen-only atmosphere are presented in figure 20, for a number of arbitrary times which illustrate the approach to photochemical equilibrium. Similar curves for atomic oxygen were also obtained, but these were omitted for brevity. Quite high O_3 values were obtained in the lower stratosphere at very early times, but the rate of increase became very slow as the O_3 concentrations built up. The integration was terminated after about 20 days because of the slowness of the response, even though equilibrium was not attained below about 35 km. The fastest response was at about 50 km, where only about 5 hr were required to reach equilibrium. At higher levels the response time increased again because of the slow growth of the atomic oxygen concentrations, as discussed by Hunt (1966b). Since the response curves in

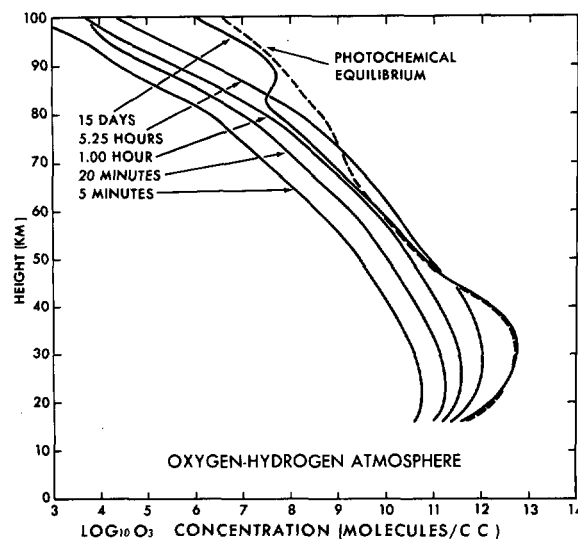


FIGURE 21.—Photochemical growth curves of the ozone concentrations for an oxygen-hydrogen atmosphere illustrating the approach to photochemical equilibrium.

figure 20 are for a fixed overhead sun shining for 24 hr a day, they represent a considerably faster response than would be obtained in the actual atmosphere. Some incomplete calculations were also made in which the diurnal variation of the sun was incorporated, and these indicated that an increase in the response times of a factor of 4 or 5 could be expected. At higher latitudes where the solar altitudes are lower, an additional increase in the response time would result. Thus the inability of the photochemistry to maintain the R4 concentrations in the Tropics, as shown in figure 16, against the action of the dynamics can be readily appreciated.

The corresponding growth curves for O_3 in an oxygen-hydrogen atmosphere are given in figure 21. These reveal the much faster response times that are obtained for this type of reaction scheme, photochemical equilibrium being virtually attained in the stratosphere down to 16 km in about 15 days for an overhead sun active 24 hr in a day. The peculiar response around 80 km was produced by the H concentrations there being temporarily greater than equilibrium, resulting in a decrease in the O_3 . The response times in this atmosphere were presumably just fast enough to counteract the dynamic changes in the Tropics, as indicated in figure 5, and thus relatively constant R3 values were maintained at low latitudes. At high latitudes where the photochemical response was slower, the photochemistry was unable to prevent an accumulation of ozone in the stratosphere.

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